On the Differences Between X-ray and Neutron Thermal Vibration Parameters

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Abstract

For crystal structures analyzed by both X-ray and neutron diffraction, the anisotropic mean-square displacement parameters of the non-H atoms are sometimes found to differ significantly. The differences can usually be adjusted by either: (1) an isotropic factor q, defined by $U_X^{ij} = qU_N^{ij}$, to correct for a temperature difference between the two experiments; (2) anisotropic factors q_{ij}, defined by $U_X^{ij} = q_{ij}U_N^{ij}$, to correct for a temperature difference and different anisotropic diffraction effects of absorption, extinction, thermal diffuse scattering, multiple reflection, or systematic measuring errors in the two experiments; (3) anisotropic diffraction correction terms ΔU^{ij}, defined by $U_X^{ij} = U_N^{ij} + \Delta U^{ij}$; (4) the sum of an isotropic temperature correction and anisotropic diffraction corrections, defined by $U_X^{ij} = qU_N^{ij} + \Delta U^{ij}$. Correction parameters q, q_{ij} and ΔU^{ij} are easily calculated by linear least-squares fit, and the corrections from (3) or (4) seem to be the most reliable. Corrections calculated from X-ray and neutron U^{ij}'s of the non-H atoms of a crystal can be useful for adjusting the neutron U^{ij}'s of the H atoms for adoption, along with the neutron coordinates of the H atoms, as fixed parameters in an X-ray analysis of the electron density distribution.

Introduction

When the same crystal structure is analyzed by both X-ray and neutron diffraction, the two analyses sometimes yield systematically different anisotropic mean-square displacement parameters* for the non-H atoms. Since X-rays are scattered by electrons, while neutrons are scattered by nuclei, the X-ray U_X^{ij} values are often found to be larger than the neutron U_N^{ij} values, and much of the

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*Throughout this paper we refer to mean-square displacement parameters U^{ij} (Å²), defined by atomic Debye–Waller factors

$$e^{-W} = \exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a^{*i} a^{*j} U^{ij}).$$

The U^{ij} form a symmetric matrix U, and the mean-square atomic displacement parallel to any unit vector n is given by

$$\langle u^2 \rangle = \mathbf{n}^T \mathbf{U} \mathbf{n} = \sum_{i=1}^{3} \sum_{j=1}^{3} n_i n_j U^{ij},$$

where n_i are the components of the column vector n along the reciprocal lattice axes a^{*i}.

difference can be attributed to the tendency of the X-ray values to fit not only the anisotropic atomic displacements due to thermal vibration, but also the nonspherical deformations of the valence electron-density distribution due to chemical bonding. When the X-ray refinement is limited to high-angle data, say $(\sin\theta)/\lambda > 0.8 \, \text{Å}^{-1}$, for which the scattering is due mainly to the spherical core electron densities, or when multipolar valence electron-density distributions are explicitly parameterized in the X-ray structure factor model, the U^{ij} differences are much smaller. In some such cases, *e.g.* a study of alloxan (Swaminathan, Craven & McMullan, 1985), the differences are indeed insignificant. However, in other cases, *e.g.* a series of studies of α-oxalic acid dihydrate (Coppens, Dam, Harkema, Feil, Feld, Lehmann, Goddard, Krüger, Helner, Johansen, Larsen, Koetzle, McMullan, Maslen & Stevens, 1984), significant differences persist, and it is not uncommon to find

$$\langle (\Delta/\sigma)^2 \rangle^{1/2} \gg 2,$$

where

$$\Delta = U_X^{ij} - U_N^{ij} \text{ and } \sigma = \sigma(\Delta) = [\sigma^2(U_X^{ij}) + \sigma^2(U_N^{ij})]^{1/2}.$$

In such cases it might be necessary – as a practical, operational matter – to adjust the neutron parameters to the X-ray parameters in order to prepare so-called *X*-minus-*N* deformation electron-density maps (*e.g.* Coppens, 1978) or to adopt fixed neutron structural parameters and then fit multipolar pseudoatom electron-density parameters to the X-ray data (*e.g.* Craven & McMullan, 1979; Klooster, Swaminathan, Nanni & Craven, 1992). A similar practical problem arises in attempts at joint X-ray and neutron refinement of structural and electron-density parameters (Coppens, Boehme, Price & Stevens, 1981).

Descriptive analysis

Differences between mean-square displacement parameters from two different diffraction analyses of the same crystal structure might be due to:

(1) *Different experimental temperatures*

Theory at various levels of approximation predicts that at sufficiently high temperatures, mean-square atomic

displacements due to thermal vibration should increase linearly with temperature. For example, in the harmonic oscillator approximation, the energy of a vibration mode with frequency ν is, according to classical mechanics,

$$E = 4\pi^2 m\nu^2 \langle u^2 \rangle,$$

or, according to quantum statistical mechanics,

$$E = h\nu\{\tfrac{1}{2} + 1/[\exp(h\nu/k_B T) - 1]\}.$$

Equating these gives

$$\langle u^2 \rangle = h/4\pi^2 m\nu\{\tfrac{1}{2} + 1/[\exp(h\nu/k_B T) - 1]\},$$

and in the low-frequency high-temperature limit with $h\nu < k_B T$

$$\langle u^2 \rangle = h/4\pi^2 m\nu(\tfrac{1}{2} + k_B T/h\nu).$$

(2) Different absorption effects

The kinematic Bragg reflection intensity

$$I_{\text{Bragg}} \propto |F|^2 ALp$$

is attenuated by the transmission factor

$$A = V^{-1} \int_v \exp[-\mu(t_0 + t_1)]\, d^3 t, \quad 0 < A < 1.$$

For spherical crystals, the transmission factor increases very nearly linearly with $(\sin\theta)^2$

$$A \simeq A_0 + A_1(\sin\theta)^2,$$

where A_0 and A_1 are functions of μR (Bond, 1967, as cited by Dunitz, 1979, p. 289). For nonspherical crystals, the transmission also varies anisotropically. In general, absorption attenuates low-angle reflections more than high-angle reflections, and uncorrected absorption biases mean-square displacement parameters toward values that are too small.

(3) Different extinction effects

To a first approximation (Darwin, 1914, as cited by Dunitz, 1979, p. 290), the extinction factor y defined by

$$I_{\text{meas}} = yI_{\text{Bragg}}, \quad y < 1,$$

falls off exponentially with the kinematic intensity

$$y \simeq \exp(-gI_{\text{Bragg}}), \quad g > 0.$$

Extinction tends to be more serious in neutron than in X-ray data, because larger specimen crystals are used for neutron measurements. Extinction can also be anisotropic (Becker & Coppens, 1975) due to anisotropy of the imperfect mosaic structure of perfect microcrystalline domains. In X-ray diffraction, extinction attenuates the strong low-angle reflections more than the weak high-angle reflections, and uncorrected extinction, like uncorrected absorption, biases the mean-square displace-

ment parameters toward values that are too small. In neutron diffraction, the effect is qualitatively similar but quantitatively different, because neutron scattering falls off more gradually with increasing scattering angle than does X-ray scattering. With both radiations, the scattering is attenuated by thermal vibration in the same way, but neutron scattering lengths do not fall off with increasing scattering angle as X-ray scattering factors do. As a result, neutron extinction effects can persist to higher scattering angles.

(4) Different thermal diffuse scattering effects

In accordance with the principle of conservation of energy for the total scattering, as the intensity of elastic Bragg scattering decreases due to destructive interference of beams scattered by atoms displaced by thermal vibration, the intensity of inelastic thermal diffuse scattering (TDS) increases due to energy exchanges between the scattered beams and the lattice vibration modes. Overall, the Bragg intensities decrease and the TDS intensities increase, approximately exponentially with $(\sin\theta)^2/\lambda^2$. If the thermal attenuation of the Bragg scattering is anisotropic, then so is the TDS (Harada & Sakata, 1974; Sakata & Harada, 1976). Here we refer to anisotropic variation of the TDS intensity from lattice point to lattice point in reciprocal space, not to the inherently anisotropic distribution of TDS intensity about a given reciprocal lattice point. The latter arises because all crystals, even those of cubic symmetry, have anisotropic mechanical elasticity.

Being inelastic, TDS increases the wavelength spread of the scattered beam. The TDS peak is, therefore, inherently broader than the Bragg peak, but both types of scattering peak at $\theta(hkl)$. Thus, depending on the reflection integration limits, some part of the TDS is included in the integrated intensity measurements, and

$$I_{\text{meas}} = I_{\text{Bragg}}(1 + \alpha),$$

where

$$\alpha = I_{\text{TDS}}/I_{\text{Bragg}}$$

and

$$\alpha_{\text{iso}} = \alpha_0(\sin\theta)^2/\lambda^2 = \alpha_0 d^{*2}/4 \text{ or } \alpha_{\text{aniso}} = (1/4)\mathbf{h}^T \alpha \mathbf{h}.$$

Thus, uncorrected TDS, like uncorrected absorption or extinction, biases the mean-square displacement parameters toward values that are too small. The necessary TDS corrections will be different in X-ray and neutron experiments due to the different intensity integration conditions, which include the different size of the specimen crystal, wavelength spread, beam divergence, aperture dimensions, scan mode and scan widths. In addition, if the speed of sound in the crystal exceeds the neutron speed, as can happen for very hard crystals, the neutron TDS peak will be flattened (Willis & Pryor, 1975).

(5) Different multiple reflection effects

Multiple reflection occurs when one or more secondary reciprocal lattice points $\mathbf{h}_m$ intersect the Ewald sphere simultaneously with the primary point of interest $\mathbf{h}$

$$I_{\text{meas}}(\mathbf{h}) = I_{\text{Bragg}}(\mathbf{h})A(\mathbf{h})y(\mathbf{h})[1 + \propto (\mathbf{h})]$$
$$+ \sum_m p_m I_{\text{Bragg}}(\mathbf{h}_m).$$

Although in principle the range of the coefficients is $-1 < p_m < +1$, in practice usually $|p_m| < 0.1$, and typically $|p_m| \simeq 0.01$, so that the effect on $I_{\text{meas}}(\mathbf{h})$ is large only if $I_{\text{Bragg}}(\mathbf{h}_m)$ is large. The general tendency is to weaken I_{meas} for strong reflections ($p_m < 0$) and strengthen it for weak ones ($p_m > 0$). Thus, like uncorrected absorption, extinction or thermal diffuse scattering, multiple reflection tends to bias the mean-square displacement parameters toward values that are too small. In X-ray experiments, multiple reflection is sometimes detected or avoided by making measurements at several azimuthal settings around the diffraction vector; in neutron experiments, such multiple measurements are usually precluded by beam-time considerations. Computational corrections (Le Page & Gabe, 1979; Coppens, 1978, and references therein) are seldom attempted.

(6) Different systematic measuring errors

Scan truncation errors may be quite common and, if uncorrected, they bias the mean-square displacement parameters toward values that are too large. These errors can arise from the long tails of a Lorentzian wavelength distribution (Denne, 1977), or from the spectral dispersion effect of a parallel-geometry monochromator, which causes reflection widths to vary as $\Delta\omega = [a + b_1 \tan\theta + b_2(\tan\theta)^2]^{1/2}$ rather than as $\Delta\omega = a + b\tan\theta$ (*e.g.* Blessing, 1987). An incident beam monochromator can also produce an inhomogeneous, quasi-parallel (as opposed to divergent) beam that illuminates the specimen crystal nonuniformly. The resulting *beam inhomogeneity errors* resemble anisotropic absorption effects (Harkema, Dam, van Hummel & Reuvers, 1980).

Quantitative comparisons

Of the several effects just described, only the temperature effect is isotropic; the effects of absorption, extinction, thermal diffuse scattering, multiple reflection and measuring errors are, in general, anisotropic.

Experimental U_X^{ij}/U_N^{ij} ratios are sometimes approximately isotropic and constant, but more often the ratios are anisotropically variable. When the ratios are about constant, it is straightforward to evaluate an isotropic scale factor q defined by

$$U_X^{ij} = qU_N^{ij}, \tag{1}$$

and estimated as $q = \langle U_X^{ij}/U_N^{ij}\rangle_{a,ij}$, where the average is taken over the indices i and j as well as over the atoms a of the crystal chemical unit. In the high-temperature limit, this also gives an estimate of the ratio of experimental temperatures, $T_X/T_N \simeq q$.

To deal with anisotropically variable ratios, some workers have used anisotropic scale factors defined by

$$U_X^{ij} = q_{ij}U_N^{ij}, \tag{2}$$

and estimated as $q_{ij} = \langle U_X^{ij}/U_N^{ij}\rangle_a$. Other workers have used separate $q_i = \langle U_X^{ii}/U_N^{ii}\rangle_a$ for the U^{ii} values, and $q = 1$, $q = (q_1 + q_2 + q_3)/3$, or $q = (q_i + q_j)/2$ for the U^{ij} values with $i \neq j$. Another possibility would be to scale the U^{ij} using $(q_i q_j)^{1/2}$, the geometric mean of q_i values derived from U^{ii}. The scaling would then correspond to a matrix multiplication

$$\mathbf{U}_X = \mathbf{q}^T \mathbf{U}_N \mathbf{q}, \quad \text{where } \mathbf{q} = \begin{pmatrix} q_1^{1/2} & 0 & 0 \\ 0 & q_2^{1/2} & 0 \\ 0 & 0 & q_3^{1/2} \end{pmatrix}.$$

Ratios of the U^{ij} with $i \neq j$ tend not to give reliable scaling factors, because the U^{ij} tend to have smaller magnitudes than the U^{ii}, and small differences between the U^{ij} can produce extreme values for their ratios. In addition, while the U^{ii} are related to the principal-axis amplitudes or eigenvalues of the mean-square displacement tensors, the U^{ij} are related to the principal-axis directions or eigenvectors, and the orientations of the root mean-square displacement ellipsoids are very sensitive to small changes in the U^{ij}, with $i \neq j$.

For equal-atom, small-molecule, well ordered crystal structures of the type usually analyzed in joint X-ray and neutron studies of electron-density distributions, the anisotropic diffraction effects described above are not expected to vary widely from atom to atom; rather, they might be expected to add a roughly constant contribution to each atom's anisotropic mean-square displacement parameters. This suggests evaluating the $U_X^{ij} - U_N^{ij}$ differences, rather than the U_X^{ij}/U_N^{ij} ratios, and anisotropic additive correction terms ΔU^{ij} defined by

$$U_X^{ij} = U_N^{ij} + \Delta U^{ij}, \tag{3}$$

rather than anisotropic scaling factors. More generally, one can consider the sum of an isotropic temperature correction and anisotropic diffraction corrections

$$U_X^{ij} = qU_N^{ij} + \Delta U^{ij}. \tag{4}$$

Temperature differences indicated by isotropic correction factors $q \neq 1$ can be confirmed by differences in unit-cell dimensions, but physical causes of anisotropic correction terms $\Delta U^{ij} \neq 0$ usually cannot be ascertained without additional or repeated diffraction measurements. The ΔU^{ij} are then simply operationally expedient numerical adjustments and they should be used with caution, because the underlying assumption that the ΔU^{ij}

should be constant from atom to atom might not hold in some cases. For example, for a heavy-atom structure, if some systematic error affects the high-angle more than the low-angle data, it will disproportionately affect the heavy-atom U^{ij} values. If such a case is suspected, the heavy-atom U^{ij} should not be used to evaluate the ΔU^{ij}.

Calculation procedures

Correction parameters q, q_{ij} and ΔU^{ij} are readily obtained by linear least-squares fit. The results corresponding to (1)–(4) are, respectively,

$$q = \sum w U_X^{ij} U_N^{ij} / \sum w (U_N^{ij})^2, \qquad (5a)$$

$$q_{ij} = \sum_a w U_X^{ij} U_N^{ij} / \sum_a w (U_N^{ij})^2, \qquad (5b)$$

$$\Delta U^{ij} = \left(\sum_a w U_X^{ij} - \sum_a w U_N^{ij} \right) \sum_a w, \qquad (5c)$$

and the normal equations solution

$$
\begin{pmatrix} q \\ \Delta U^{11} \\ \Delta U^{22} \\ \vdots \\ \Delta U^{23} \end{pmatrix}
$$

$$
= \begin{pmatrix}
\sum_a w (U_N^{ij})^2 & \sum_a w U_N^{11} & \sum_a w U_N^{22} & \cdots & \sum_a w U_N^{23} \\
\sum_a w U_N^{11} & \sum_a w & 0 & \cdots & 0 \\
\sum_a w U_N^{22} & 0 & \sum_a w & \cdots & 0 \\
\vdots & \vdots & \vdots & & \vdots \\
\sum_a w U_N^{23} & 0 & 0 & \cdots & \sum_a w
\end{pmatrix}^{-1}
$$

$$
\times \begin{pmatrix}
\sum w U_X^{ij} U_N^{ij} \\
\sum_a w U_X^{11} \\
\sum_a w U_X^{22} \\
\vdots \\
\sum_a w U_X^{23}
\end{pmatrix}. \qquad (5d)
$$

In these equations, the symbol $\sum_a$ denotes the single summation $\sum_{a=1}^{n}$ over the n atoms in the crystal chemical unit for fixed values of the indices i and j; otherwise, the symbol $\sum$ denotes the triple summation $\sum_{a=1}^{n} \sum_{i=1}^{3} \sum_{j=i}^{3}$ over the n atoms and the six ($i < j = 1, 2, 3$) mean-square displacement parameters of each atom.

The least-squares fitting minimizes χ^2 residuals

$$\chi_k^2 = \sum w \Delta_k^2 = \sum (\Delta_k / \sigma)^2, \qquad (6)$$

where $k = 0, 1, 2, 3, 4$, and

$$\Delta_0 = U_X^{ij} - U_N^{ij}, \qquad (7a)$$

$$\Delta_1 = U_X^{ij} - U_N^{ij} q, \qquad (7b)$$

$$\Delta_2 = U_X^{ij} - U_N^{ij} q_{ij}, \qquad (7c)$$

$$\Delta_3 = U_X^{ij} - U_N^{ij} - \Delta U^{ij}, \qquad (7d)$$

$$\Delta_4 = U_X^{ij} - U_N^{ij} q - \Delta U^{ij}. \qquad (7e)$$

The residual (7a) corresponds to the unadjusted mean-square displacement parameters, and (7b)–(7e) correspond to the results (5a)–(5d), respectively. Since we expect $q \simeq 1$ and $\Delta U^{ij} \simeq 0$, we employ weights $w = 1/\sigma^2$ with

$$\sigma = \sigma(\Delta) = \sigma(U_X^{ij} - U_N^{ij}) = [\sigma^2(U_X^{ij}) + \sigma^2(U_N^{ij})]^{1/2}. \qquad (8)$$

If the results are far from $q \simeq 1$ and $\Delta U^{ij} \simeq 0$, they can be used to adjust $\sigma(U_N^{ij})$ to $\sigma(U_X^{ij})$ to obtain better weights for a recalculation. Useful agreement statistics are the weighted root mean-square errors of fit

$$\langle \Delta_k^2 \rangle^{1/2} = [\chi_k^2 / \sum w]^{1/2}, \qquad (9)$$

and the reduced χ^2 values

$$Z_k = [\chi_k^2 / (6n - m_k)]^{1/2}, \qquad (10)$$

where, for $k = 0, 1, 2, 3$ and 4, the numbers of variable parameters are $m_k = 0, 1, 6, 6$ and 7, respectively.

Since ΔU^{ij} must apply to the unit-cell averages of U^{ij} as well as to U^{ij} of each atom, they should obey the symmetry restrictions given in Table 1. Conformity to these restrictions is a test of physical plausibility of the fitted ΔU^{ij} values.

Sample calculations

Illustrative calculations were performed using the U^{ij}'s of the non-H atoms of α-oxalic acid dihydrate from the IUCr project on comparison of structural parameters and electron-density maps (Coppens et al., 1984). The project involved nine independent data sets, four X-ray and five neutron, measured at nominal temperatures ranging from 75 to 115 K.*

Agreement statistics, defined by (9) and (10), are given in Table 2 for the X/X and N/N as well as the X/N inter-experiment comparisons. Among the 36 pairwise comparisons, there was no case in which the one-parameter, isotropic q model (1) gave the best fit; in nine cases, the six-parameter q_{ij} model (2) was best; in six cases, the six-parameter ΔU^{ij} model (3) was best; and, in the

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*Parameters from the four high-angle X-ray refinements and the five neutron refinements, and the FORTRAN program used to calculate the least-squares correction parameters and agreement statistics have been deposited with the IUCr (Reference: CR0481). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Symmetry restrictions on ΔU^{ij} correction terms*

Triclinic	None
Monoclinic	$\Delta U^{12} = \Delta U^{23} = 0$
Orthorhombic	$\Delta U^{12} = \Delta U^{23} = \Delta U^{13} = 0$
Tetragonal	$\Delta U^{11} = \Delta U^{22}$, $\Delta U^{12} = \Delta U^{23} = \Delta U^{13} = 0$
Rhombohedral	None
Hexagonal	$\Delta U^{11} = \Delta U^{22}$, $\Delta U^{12} = \Delta U^{11}/2$, $\Delta U^{23} = \Delta U^{13} = 0$
Cubic	$\Delta U^{11} = \Delta U^{22} = \Delta U^{33}$, $\Delta U^{12} = \Delta U^{23} = \Delta U^{13} = 0$

remaining 21 cases, the seven-parameter $q + \Delta U^{ij}$ model (4) was best. Failure of the isotropic q model to give a good fit indicates that experimental temperature differences alone do not account for the U^{ij} differences. Among the nine cases in which the anisotropic q_{ij} model gave the best fit, there were only three – namely, $X1/X2$, $X1/X3$ and $X1/X4$ – in which it was significantly better than the ΔU^{ij} or $q + \Delta U^{ij}$ model. The questionable reliability of q_{ij} scaling factors with $i \neq j$ was illustrated by the $N3/N4$ case: Although the q_{ij} model gave the best fit, q_{23} was, unreasonably, more than twice the q_{ii} values. In general, the ΔU^{ij} from (3) or (4) probably provide more reliable anisotropic corrections than q_{ij} from (2), even if (2) gives a slightly better fit. The q and ΔU^{ij} values from (4) are listed in Table 3, and the q values are compared with the reported experimental temperatures in Table 4.

Comparisons with experiment $X4$ gave values of Z_0 (Table 2) and q (Table 3) very different from unity. This is largely because Dirac–Slater form factors were used in the $X4$ refinement, while relativistic Hartree–Fock form factors were used in the other X refinements. The Dirac–Slater form factors represent more compact atoms, and therefore should – other things being equal – produce larger U^{ij} values (Coppens et al., 1984). The effect was particularly pronounced for the U^{22} values, which correspond to atomic displacements perpendicular to the plane of the oxalic acid molecule. The Z_0 and q values were also far from unity for comparisons with experiment $N3$; this is due largely to its lower temperature of 75 K compared with 100–115 K for the other experiments. The common occurrence of $Z_k < 1$ for comparisons with experiment N5 suggest that its $\sigma(U^{ij})$ values, which were twice or more as large as those of the other N experiments, were overestimated. The large values of ΔU^{33} for comparisons with experiment $X1$ indicate that its U^{33} were systematically overestimated, perhaps due to correlation with the anisotropic extinction correction applied in the $X3$ refinement. The reported lower temperature of 75 K for experiment $N3$ is borne out by the fitted q values (Table 4), but the reported higher temperature of 115 K for experiment $N5$ is not.

Overall, the fitting procedure was able to reduce the root mean-square U^{ij} differences by factors of ca 2–20. The residual differences $\langle \Delta^2 U^{ij} \rangle^{1/2} \simeq 0.0001$–$0.0005$ Å represent some 1–5% of $\langle U_{iso} \rangle \simeq 0.012$ Å^2, where $\langle U_{iso} \rangle$ is the average of the U^{ii} values from the nine experiments. These results show that the fitting proce-

Table 2. *Statistics* of inter-experiment fitting of U^{ij} of the non-H atoms of α-oxalic acid dihydrate (Coppens et al., 1984)*

Expt. Pair	Z_0	Z_1	Z_2	Z_3	Z_4	$\langle \Delta_m^2 \rangle^{1/2}$ (Å^2)	$\langle \Delta_4^2 \rangle^{1/2}$ (Å^2)
$X1/N1$	7.75	5.09	<u>1.38</u>	1.46	1.45	0.00024	0.00024
$N2$	5.40	3.70	1.39	<u>1.37</u>	1.37	0.00028	0.00027
$N3$	9.65	3.66	1.64	2.60	<u>1.58</u>	0.00036	
$N4$	7.00	4.02	3.40	<u>2.55</u>	2.56	0.00044	0.00043
$N5$	2.69	2.56	<u>0.55</u>	0.63	0.65	0.00022	0.00025
$X2/N1$	7.22	2.18	1.19	1.67	<u>0.78</u>	0.00007	
$N2$	3.53	1.69	1.13	1.23	<u>0.84</u>	0.00011	
$N3$	10.39	1.84	1.44	3.69	<u>1.17</u>	0.00019	
$N4$	10.04	8.90	6.00	<u>5.01</u>	5.11	0.00043	0.00043
$N5$	0.68	0.68	0.27	0.26	<u>0.18</u>	0.00006	
$X3/N1$	10.52	3.35	1.61	2.04	<u>1.13</u>	0.00011	
$N2$	6.10	2.76	1.30	1.58	<u>1.02</u>	0.00015	
$N3$	12.50	2.06	1.54	3.71	<u>1.28</u>	0.00022	
$N4$	12.44	10.35	5.69	<u>4.55</u>	4.67	0.00046	0.00046
$N5$	1.54	0.86	0.36	0.45	<u>0.29</u>	0.00010	
$X4/N1$	20.89	3.73	1.25	5.14	<u>0.90</u>	0.00012	
$N2$	15.84	2.90	1.27	4.14	<u>1.21</u>	0.00021	
$N3$	19.49	2.05	1.65	6.17	<u>1.38</u>	0.00028	
$N4$	20.95	8.87	5.45	5.85	<u>4.98</u>	0.00068	
$N5$	6.72	1.68	<u>0.41</u>	1.93	0.45	0.00016	0.00017
$X1/X2$	5.54	5.30	<u>1.04</u>	1.45	1.43	0.00018	0.00023
$X3$	5.96	6.07	<u>0.98</u>	1.61	1.48	0.00018	0.00026
$X4$	11.75	5.10	<u>0.96</u>	3.68	1.41	0.00019	0.00027
$X2/X3$	4.28	2.28	1.08	1.18	<u>1.06</u>	0.00009	
$X4$	17.29	1.90	0.78	4.40	<u>0.75</u>	0.00010	
$X3/X4$	13.57	1.71	<u>0.90</u>	3.67	0.97	0.00013	0.00014
$N1/N2$	2.23	1.66	0.95	<u>0.66</u>	0.67	0.00010	0.00009
$N3$	6.39	1.77	1.13	2.73	<u>1.09</u>	0.00018	
$N4$	6.18	6.20	4.32	4.48	<u>4.25</u>	0.00040	
$N5$	1.91	0.62	0.30	0.27	<u>0.18</u>	0.00006	
$N2/N3$	6.52	1.48	<u>1.10</u>	2.30	1.13	0.00023	0.00023
$N4$	4.35	4.36	3.50	3.01	<u>2.83</u>	0.00040	
$N5$	1.41	0.93	0.33	0.34	<u>0.28</u>	0.00010	
$N3/N4$	6.77	3.01	<u>1.83</u>	3.66	2.07	0.00032	0.00035
$N5$	4.62	0.90	0.43	1.32	<u>0.42</u>	0.00016	
$N4/N5$	2.71	2.07	1.25	<u>1.15</u>	1.18	0.00041	0.00041
Score	0	9	6	21			

*The tabulated value of $\langle \Delta_m^2 \rangle^{1/2}$ corresponds to the minimum value of Z_k, which is underscored. For the cases in which Z_4 from the fit to (4) was not the minimum, $\langle \Delta_4^2 \rangle^{1/2}$ is also tabulated. The tabulated quantities are defined by

$$Z_k = [x_k^2/(6n - m_k)]^{1/2} \quad \text{and} \quad < \Delta_k^2 >^{1/2} = [x_k^2/ \textstyle\sum w]^{1/2}$$

where

$$\chi_k^2 = \sum w \Delta_k^2 = \sum (\Delta_k/\sigma)^2;$$

$$k = 0, 1, 2, 3, 4;$$

$$\Delta_0 = U_X^{ij} - U_N^{ij} \qquad , \quad m_0 = 0;$$
$$\Delta_1 = U_X^{ij} - U_N^{ij}q \qquad , \quad m_1 = 1;$$
$$\Delta_2 = U_X^{ij} - U_N^{ij}q_{ij} \qquad , \quad m_2 = 6;$$
$$\Delta_3 = U_X^{ij} - U_N^{ij} - \Delta U^{ij} \qquad , \quad m_3 = 6;$$
$$\Delta_4 = U_X^{ij} - U_N^{ij}q - \Delta U^{ij} \qquad , \quad m_4 = 7;$$

$$w = 1/\sigma^2; \quad \sigma = \sigma(\Delta) = \sigma(U_X^{ij} - U_N^{ij}) = [\sigma^2(U_X^{ij}) + \sigma^2(U_N^{ij})]^{1/2}.$$

dure can provide statistically sound, and physically sensible, corrections for adjusting neutron U^{ij} values for adoption as fixed parameters in X-ray analyses of electron-density distributions.

Table 3. *Inter-experiment correction parameters** q (dimensionless) and ΔU^{ij} ($\text{Å}\times10^5$) from the fit to (4)*

Expt. Pair	q	ΔU^{11}	ΔU^{22}	ΔU^{33}	ΔU^{12}	ΔU^{13}	ΔU^{23}
X1/N1	1.04	58	157	323	−24	19	−7
N2	1.03	76	81	265	−34	−4	−23
N3	1.30	119	89	337	−27	54	−16
N4	0.95	158	324	258	−21	67	2
N5	1.00	−48	56	304	−26	−31	−6
X2/N1	1.08	15	96	21	−17	21	−3
N2	1.07	33	15	−39	−26	−3	−18
N3	1.36	68	12	23	−22	56	−14
N4	0.96	143	299	−23	−6	79	8
N5	1.04	−98	−14	0	−19	−32	−2
X3/N1	1.11	71	187	14	−19	17	−6
N2	1.11	86	97	−49	−29	−7	−23
N3	1.40	128	107	19	−22	54	−16
N4	0.99	206	403	−25	−5	80	3
N5	1.07	−46	70	−7	−20	−36	−6
X4/N1	1.42	44	330	48	−10	14	0
N2	1.41	70	228	−28	−21	−15	−20
N3	1.82	97	194	38	−20	56	−13
N4	1.25	224	622	4	10	92	15
N5	1.38	−120	162	12	−14	−59	2
X1/X2	0.96	40	62	303	−7	−2	−5
X3	0.94	−10	−19	312	−5	2	−1
X4	0.73	26	−85	290	−16	9	−8
X2/X3	0.97	−50	−81	13	2	6	3
X4	0.76	−18	−156	−16	−10	11	−3
X3/X4	0.78	42	−63	−20	−11	8	−7
N1/N2	1.00	17	−76	−55	−8	−22	−14
N3	1.27	47	−79	0	−4	32	−10
N4	0.91	108	172	−46	9	51	10
N5	0.96	−105	−103	−19	−2	−50	1
N2/N3	1.27	36	5	59	5	55	5
N4	0.91	96	256	16	19	75	26
N5	0.96	−114	−17	41	8	−26	15
N3/N4	0.75	18	159	−67	4	7	15
N5	0.75	−114	−12	−7	4	−63	8
N4/N5	0.99	−160	−206	78	4	−89	−11

*Since the crystal structure is monoclinic, the condition $\Delta U^{12} = \Delta U^{23} = 0$ should hold, and generally it does, to within $\sigma(\Delta) = [\sigma^2(U_X) + \sigma^2(U_N)]^{1/2}$.

Table 4. *Reported (Coppens et al., 1984) experimental temperatures (K) and q values (dimensionless) from the fit to (4)*

Expt.		X1	X2	X3	X4	N1	N2	N3	N4	N5
T		100	100	103	100	100	100	75	100	115
X1	100	1.00	0.96	0.94	0.73	1.04	1.03	1.30	0.95	1.00
X2	100		1.00	0.97	0.76	1.08	1.07	1.36	0.96	1.04
X3	103			1.00	0.78	1.11	1.11	1.40	0.99	1.07
X4	100				1.00	1.42	1.41	1.82	1.25	1.38
N1	100					1.00	1.00	1.27	0.91	0.96
N2	100						1.00	1.27	0.91	0.96
N3	75							1.00	0.75	0.75
N4	100								1.00	0.99
N5	115									1.00

Adjusted U^{ij}'s for H atoms

It is well known that neutron diffraction gives mean positions and mean-square displacements for H atoms that are much more accurate than those from X-ray diffraction. This is true even if the neutron data are of only moderate precision and relatively low resolution – say $\langle\sigma(|F|)\rangle/\langle|F|\rangle \simeq 0.05$ or more, and $(\sin\theta_{max})/\lambda \simeq 0.5\,\text{Å}^{-1}$ or less – and the X-ray data are high-precision, high-resolution data measured for an

electron-density analysis – typically $\langle\sigma(|F|)\rangle/\langle|F|\rangle \simeq 0.02$ or less, and $(\sin\theta_{max})\lambda \simeq 1\,\text{Å}^{-1}$ or more. This being so, the most valuable application of the corrections calculated from the X-ray and neutron U^{ij}'s of the non-H atoms of a crystal might be adjustment of the neutron U^{ij}'s of the H atoms.

If the ΔU^{ij} model (3) gives a good fit for the non-H atoms, then application to the H atoms is straightforward, and

$$U_X^{ij}(H) = U_N^{ij}(H) + \Delta U^{ij}(\text{non-H}) \qquad (11a)$$

is a reasonable approximation. If, however, the $q + \Delta U^{ij}$ model (4) gives a q value significantly different from unity, thus indicating significantly different experimental temperatures, then the application is more complicated. This is because a large part of the mean-square displacement of H atoms is due to their zero-point motions in bond-stretching and bond-bending internal vibration modes, which, on account of the small mass of H atoms, have amplitudes comparable to those of lattice vibration modes. Since the zero-point vibrations are temperature-independent, the internal vibration amplitudes do not scale with temperature as do the lattice vibration amplitudes. A proper correction based on (4) would then be

$$U_X^{ij}(H) = q[U_N^{ij}(H) - U_0^{ij}(H)] + U_0^{ij}(H) + \Delta U^{ij}, \qquad (11b)$$

where $U_0^{ij}(H)$ represent mean-square internal vibration amplitudes transformed from local Cartesian axes at each H atom to the crystallographic axes. Internal vibration amplitudes for C—H, N—H and O—H H atoms from a sampling of spectroscopic and neutron diffraction studies are compiled in Table 5.

Finally, we note very recent studies by Chen & Craven (1995) showing that differences between X-ray and neutron U^{ij}'s for non-H atoms can be fitted by a pseudoatom model for the electronic charge-density distribution in the X-ray refinement. The dimensionless radial scaling parameters κ, which are intended to model contraction or expansion of bound pseudoatoms as compared with free atoms (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979*), are most effective in this regard. X-ray U^{ij}'s change significantly according to whether κ's are set to unity, set to some standard value, or are unconstrained; joint refinement of U^{ij} and κ parameters can significantly improve agreement between X-ray and neutron U^{ij}'s. These observations raise the question: To what extent do the κ's describe atomic contractions or expansions, and to what extent are they biased by effects of thermal vibration, absorption,

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* In this paper, κ in equation (6b) should be replaced by $\kappa\alpha$, and the references to $\kappa = 1.4$ for H atoms in the discussion on pp. 65–67 should refer to $\kappa\zeta = 1.4\,\text{bohr}^{-1}$, where $\kappa\zeta$ is the exponential coefficient in the radial wavefunction for a spherically contracted H atom. This corresponds to an exponential coefficient $\kappa\alpha = 2\pi\zeta = 2.8\,\text{bohr}^{-1}$ in the radial density function.

Table 5. *Mean-square amplitudes* ($\mathring{A}^2$) *for internal vibrations of* H *atoms from spectroscopic and neutron diffraction studies of* C—H, N—H *and* O—H *bond stretching and bond bending*

		Stretch	Bend		Ref.
			In-plane	Out-of-plane	
C—H					
Methylene chloride	CH_2Cl_2	0.00578	0.01369	0.01369	(a)
Cyclobutane	C_4H_8	0.0069	0.0289	0.0139	(b)
Benzene	C_6H_6	0.0059	0.0135	0.0225	(b)
Formamide	$HCONH_2$	0.0057	0.0115		(c)
Acetamide	CH_3CONH_2	0.0058		0.0144	(d)
Monofluoroacetamide	FCH_2CONH_2	0.0055	0.0213	0.0142	(e)
Formamide oxime	$\overset{\text{NOH}}{\overset{\|}{HCNH_2}}$	0.0046	0.0132		(f)
N,N'-Diformohydrazine	$\overset{O}{\overset{\|}{HCNH-NH\underset{\|}{\underset{O}{CH}}}}$	0.0053	0.0121		(g)
Glyoxime	$\overset{NOH}{\overset{\|}{HC-\underset{\|}{\underset{NOH}{CH}}}}$	0.0064	0.0128	0.0044	(h)
1,2,4-Triazole	$HN-N \ldots HC \ CH$	0.0067	0.0125	0.0040	(i)
γ-Aminobutyric acid	$NH_2(CH_2)_3CO_2H$	0.0063	0.023	0.014	(j)
N—H					
Formamide		0.005	0.015		(c)
Acetamide		0.0058	0.0110		(d)
Monofluoroacetamide		0.0058	0.0130		(e)
N-Methylacetamide	$CH_3CONHCH_3$	0.005	0.015	0.027	(k)
Urea	H_2NCONH_2	0.0053	0.014	0.027	(l)
Formamide oxime		0.0058	0.0125		(f)
N,N'-Diformohydrazine		0.0055	0.0110		(g)
1,2,4-Triazine		0.0070	0.0075		(i)
O—H					
Water	av. $\langle u_H^2 \rangle - \langle u_O^2 \rangle$ in crystalline hydrates	0.0055	0.025	0.020	(m)
Formamide oxime		0.0048	0.0106	0.0081	(f)
Glyoxime		0.0048	0.0104	0.0104	(h)
Erythritol	$\overset{OH}{\overset{\|}{HOCH_2CHCHCH_2OH}}\underset{\|}{\underset{OH}{}}$	0.0058	0.0164	0.0130	(n)

References: (a) Ellison, Johnson & Levy (1971); (b) Johnson (1970); (c) Eisenstein (1979); (d) Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople (1980); (e) Jeffrey, Ruble, McMullan, DeFrees & Pople (1981a); (f) Jeffrey, Ruble, McMullan, DeFrees & Pople (1981b); (g) Jeffrey, Ruble, McMullan, DeFrees & Pople (1982); (h) Jeffrey, Ruble & Pople (1982); (i) Jeffrey, Ruble & Yates (1983); (j) Craven & Swaminathan (1984); (k) Hirshfeld & Hope (1980); (l) Ishii & Scheringer (1979); (m) Eriksson & Hermansson (1983); (n) Ceccarelli, Jeffrey & McMullan (1980).

extinction, multiple reflection, thermal diffuse scattering or systematic measuring errors, as described above?

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Molecular Conformations and Crystal Packing Properties of Five 4-Alkyl-N-(4-cyanophenyl)piperidines by X-ray Diffraction: a Surprising Dependence upon Alkyl Chain Length

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Abstract

The molecular structure and crystal packing of a homologous series of 4-n-alkyl-N-(4-cyanophenyl)piperidines (I), where alkyl equals butyl, pentyl, hexyl, heptyl and octyl ($n = 4$–8), have been analyzed. Although the conformations of the (cyanophenyl)piperidyl unit remain fairly constant throughout, the crystal packing depends acutely upon alkyl chain length with one, two or four molecules comprising the asymmetric unit: for (I) ($n = 4$), monoclinic ($P2_1$); for (I) ($n = 5$), monoclinic ($P2_1/c$); for (I) ($n = 6$), triclinic ($P\bar{1}$); for (I) ($n = 7$), triclinic ($P\bar{1}$); for (I) ($n = 8$), monoclinic ($P2_1/c$). The piperidyl rings are in a chair conformation. Unit-cell and other crystal data are presented.

Introduction

It is known that *trans*-1-n-alkyl-4-(4-cyanophenyl)cyclohexanes form monotropic smectic and enantiotropic nematic mesophases between the temperatures of the crystal and liquid phases (Eidenschink, Erdman, Krause & Pohl, 1977). To determine the influence of the isoelectronic substitution of C—H by nitrogen at the juncture between the phenyl and cyclohexyl rings, we have synthesized a series of 4-n-alkyl-N-(4-cyano-phenyl)piperidines, (I) ($n = 4$–8). Surprisingly, only (I) ($n = 6$) is mesogenic and becomes (monotropic) nematic when cooled from the liquid state. In other work, we have shown that mesomorphism can be induced by mixing homologues of (I) (Sheikh-Ali & Weiss, 1991, 1994). In order to explore possible links between the lack of liquid crystallinity in (I) and modes of packing in the solid state, the crystal structures have been analyzed and compared with each other and with their cyclohexyl analogues.

Experimental

Table 1 lists the experimental conditions and the final refinement parameters for (I) ($n = 4$–8). Samples of (I) (Sheikh-Ali & Weiss 1991, 1994) were recrystallized from hexane and affixed to a glass fiber by epoxy resin (sans hardener). Data were collected on a Siemens P4/RA diffractometer with an LT-2 low-temperature device. No phase transitions were detected by differential scanning calorimetry between room temperature and 203 K. The phase problem was solved, in some cases with difficulty, by standard direct methods, or integrated Patterson search methods (PATSEE; Sheldrick, 1985). The structures were developed by difference-Fourier calculations interspersed with cycles of full-matrix least-